# Simultaneous separation of actinides and technetium from large volumes of natural water for their determination

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#### Abstract

Monitoring of radionuclide concentration in natural samples is important for assessing environmental safety. The low concentration of long-lived radionuclides require concentration from large volumes of natural water samples. This paper presents a method for sequential separation and simultaneous determination of radioisotopes of U, Pu, Am and Tc in water samples. Actinides and technetium were pre-concentrated by coprecipitation with iron hydroxides from the aqueous sample. Separation of actinides and Tc was achieved by extraction chromatography. The developed method allows separation of actinide and technetium from 100 L water with chemical yields between 40 and 70%.

Keywords Chemical separation  $\cdot$  Actinides  $\cdot$  Technetium  $\cdot$  Coprecipitation  $\cdot$  Large volume of water  $\cdot$  Environmental radioactivity

# Introduction

Large amounts of radionuclides have been released into the environment as a result of nuclear weapons tests, nuclear accidents, nuclear fuel reprocessing, as well as other nuclear facilities as effluents. These radionuclides were transported and deposited in the seas and lakes through precipitation and river runoff. Among these radionuclides, the long-lived actinides such as isotopes of uranium (<sup>236</sup>U, <sup>233</sup>U) and plutonium (<sup>239</sup>Pu, <sup>240</sup>Pu), <sup>237</sup>Np, <sup>241</sup>Am and fission products (e.g. <sup>99</sup>Tc) are important, because of their long-residence time in the ecosystem and therefore high radiation impact. Meanwhile, these radionuclides are also useful for the investigation of environmental processes as tracers, such as water mass interaction and circulation, sedimentation of suspending particles in the ocean and lakes, dating of the sediment, soil erosion. For these purposes, reliable analytical methods

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are necessary for accurate radionuclide determination. Due to the low activity of these radionuclides in the environment, especially in seawater and fresh water samples, these radionuclides have to be preconcentrated from the large size of sample, e.g. >100 L water, meanwhile, all matrix elements and all interfering isotopes and radionuclides have to be removed before measurement. Most of the reported methods for the determination of plutonium and uranium isotopes, <sup>241</sup>Am and <sup>99</sup>Tc focused on single element/radionuclide, methods for simultaneously separation of all these radionuclides from a single sample is not available.

Large volumes of samples and preconcentration are required because of the long-lived radionuclides low concentration in the natural water. In addition, uranium, plutonium and technetium are often present in several chemical species in the environment. A number of methods have been reported for the determination of <sup>238,239,240</sup>Pu, <sup>237</sup>Np, <sup>241</sup>Am and <sup>99</sup>Tc in natural water samples only separately. Most of these methods showed relative low chemical yield of 30–60% [1].

Among others, the coprecipitation methods are fast, easy to be used in the field [2], and demonstrate high yields for radionuclides separation. All methods have some advantages and disadvantages. The following techniques are usually used for actinides separation: coprecipitation with  $Fe(OH)_3$  [3–5], this well known method shows stable and



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high yields; coprecipitation with iron hydroxide enhanced by the reducing agent Ti<sup>2+</sup>, followed by lanthanum fluoride coprecipitation [1]; coprecipitation with calcium phosphate [6], the method demonstrates high chemical yield for actinide separation (Am, U more than 70%, Pu - 50%), but it is suitable only for small volumes [6]; precipitation with manganese dioxide [7-9], the method usually shows not stable yields for the big amount of the sample. Other methods can be used for technetium separation and concentration: evaporation [10], suitable preconcentration method for small samples with low amounts of dissolved salts; sorption on activated carbon [11], very expensive method for the water routine analyses; coprecipitation with Fe(OH)<sub>2</sub> [12], as a source of iron(II) one can use either FeCl<sub>3</sub>, which is reduced simultaneously with technetium, or FeSO<sub>4</sub> which itself serves as a reducing agent. After coprecipitation, the precipitate is separated, iron and technetium are oxidized to  $Fe^{+3}$  and  $Tc^{+7}$ ,  $Fe^{+3}$  is precipitated in the form of  $Fe(OH)_3$ and separated. The chemical yield of technetium separation is 50-80% [13]. An important analytical task was to combine the methods for separating actinides and technetium in one procedure so that both of them would work well.

Long-lived actinides are mainly alpha-emitting radionuclides and can be measured using alpha-spectrometry. The actinides and Tc content in seawater are usually very low, that is why for accurate detection of actinides and Tc with low concentrations, mass-spectrometry methods (ICP-MS, AMS, TIMS, RIMS) are applied [9, 12, 14-16]. For ICP-MS, the <sup>99</sup>Tc detection limit is equivalent to 7.5 mBg  $L^{-1}$ [13]. The liquid scintillation counting (LSC) method has high detection limit and does not allow its use for the analysis of natural objects, the detection limit is  $600 \text{ mBq/m}^3$  for 200 L of water [17]. which is higher than the average technetium content in the background territories [18]. For the actinides, using ICP-MS method determination the detection limits reached to 0.55 fg mL<sup>-1</sup> for <sup>239</sup>Pu, 0.09 fg mL<sup>-1</sup> for <sup>240</sup>Pu [19],  $7.2 \times 10^{-16}$  g g<sup>-1</sup> [20] and 0.091 fg g<sup>-1</sup> for <sup>241</sup>Am [21].

Since the low concentration of these radionuclides in natural water, huge size of the sample is required for the determination of all these radionuclides, which causes a high cost for sampling, transportation of samples and long analytical time. This work aims to develop a method for simultaneous separation of Pu, Am, U, and Tc from large volume of single natural water samples. We aimed to determine the isotopes of U and Pu, Am and Tc in fresh water and seawater samples in order to investigate their level and distribution in fresh and marine water. This was to understand the impact of the anthropogenic nuclear legacy on the environment.

### **Experimental**

#### Samples and chemicals.

Standard solutions of ammonium pertechnetate (NH<sub>4</sub><sup>99</sup>TcO<sub>4</sub>), <sup>233</sup>U(VI) nitrate (<sup>233</sup>UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>), <sup>239</sup>Pu nitrate and <sup>241</sup>Am(III) nitrate (<sup>241</sup>Am(NO<sub>3</sub>)<sub>3</sub>), were purchased commercially from RITVERC JSC (Saint-Petersburg, Russia), then the solutions were diluted with milli-Q water to the following concentraitions 240 Bq mL<sup>-1</sup>, 690 ng mL<sup>-1</sup> for  $^{99}$ Tc, 1700 Bq mL<sup>-1</sup>, 8300 ng mL<sup>-1</sup> for  $^{233}$ U, 900 Bq mL<sup>-1</sup>, 390 ng mL<sup>-1</sup> for <sup>239</sup>Pu, 9500 Bg mL<sup>-1</sup>, 133 ng mL<sup>-1</sup> for <sup>241</sup>Am. Final specific activity for the solutions were measured by liquid scintillation counting (LSC) for <sup>99</sup>Tc, <sup>233</sup>U, <sup>239</sup>Pu, <sup>241</sup>Am. All reagents used in the experiments were of analytical grade, their solutions were prepared using milli-O water. 99mTc tracer for real water samples was obtained from 2 to 4 GBq commercial <sup>99</sup>Mo-<sup>99m</sup>Tc generators (Obninsk, RF). Eichrom TEVA and TRU extraction chromatographic resins with 50-100 µm particle size were purchased as 2 mL cartridges with 0.35 and 0.37 g mL<sup>-1</sup> bulk density respectively from Acrus. Anion exchange chromatography resin DOWEX 1×8-200 in chloride form with 100-200 mesh was purchased from Acrus.

The simulated sea and freshwater (Table 1) for experiments were prepared on the basis of data on the real compositions of natural water [22, 23]. For this purpose salts with nessesary cations and anions (NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·H<sub>2</sub>O, NaHCO<sub>3</sub>, KCl, KBr, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>, SrCl<sub>2</sub>, NaF, CaSO<sub>4</sub>, MgSO<sub>4</sub>·7H<sub>2</sub>O) were dissolved with milli-Q water in volumetric flasks in random order. Solutions were kept in volumetric flasks with stopper to avoid evaporation of the water and precipitaion forming. pH of the sea water solution was 8.5 and pH of the fresh water solution was 7.3.

Separation of  $^{99}$ Tc using Anion exchange column (Method I).

Simulated sea and freshwater (500 mL) was taken to a beaker and acidified to pH 2 using HCl, 25 Bq  $^{99}$ Tc was spiked with pipette. 5 g of FeSO<sub>4</sub>·7H<sub>2</sub>O was added to the

Table 1 Compositions of solutions simulating sea and fresh water

Ion	Sea water, $\times 10^{-3}$ M	Freshwater, $\times 10^{-3}$ M	
Na <sup>+</sup>	507	0.57	
$K^+$	8.7	0.03	
Mg <sup>2+</sup>	52.2	0.25	
Ca <sup>2+</sup>	10.1	0.17	
Sr <sup>2+</sup>	0.08	-	
Cl-	591	0.27	
$SO_4^{2-}$	24.8	0.42	
HCO <sub>3</sub> <sup>-</sup>	2.0	0.57	
Br <sup>-</sup>	0.74	-	
H <sub>3</sub> BO <sub>3</sub>	0.37	-	
$F^-$	0.07	-	

sample (Fe<sup>2+</sup> 10 g L<sup>-1</sup>) to reduce Tc<sup>+7</sup> to Tc<sup>+4</sup>. Ammonia solution was used to adjust pH 8-9, controlled with universal pH indicator paper, the formed precipitate (Fe(OH)<sub>2</sub> with Tc was separated by filtration on a paper filter, with the size of pore  $2-3 \mu m$ , and washed with water three times with 5-10 mL. The precipitate was dissolved with 2 mL of concentrated HCl, 10 mL of 37% H<sub>2</sub>O<sub>2</sub> solution was added to convert technetium. Concentrated ammonia was added to the sample solution, and the formed precipitate Fe(OH)<sub>3</sub> was separated by filtration on a paper filter, which was washed with water. TcO<sub>4</sub><sup>-</sup> remained in the supernatant was further separated by anion exchange chromatography using DOWEX 1×8 column (200 mesh, 2 mL column) which was conditioned with distilled water, after rinsing with 20 mL of distilled water, <sup>99</sup>Tc on the column was eluted with 20 mL of 10 M HNO<sub>3</sub> solution. The procedure is shown schematically in Fig. 1.

## Separation of<sup>99</sup>Tc using TEVA column (method II).

The simulated water (500 mL) was taken to a beaker and acidified to pH 2-3 using HCl, 25 Bq of <sup>99</sup>Tc was spiked. 4 mg of Fe<sup>3+</sup> was added and 0.25 g of reducing agent  $K_2S_2O_5$  (0.5 g L<sup>-1</sup>) were added and well mixed. NaOH solution (6 M) was added to the sample solution to adjust pH values to 8-9 controlled with universal pH indicator paper, the formed Fe(OH)<sub>2</sub> precipitate was separated by filtration, and the filter was washed with water. The precipitate was then dissolved with concentrated HCl and 0.5 g of reducing agent  $K_2S_2O_5$  (1 g L<sup>-1</sup>) was added to reduce  $TcO_4^-$  to  $Tc^{4+}$ , NH<sub>3</sub> was added to adjust pH 8–9, the formed Fe(OH)<sub>2</sub> precipitate with Tc<sup>4+</sup> was filtered on a paper filter (pore size 2-3 µm). The precipitate was dissolved with concentrated HCl. 30%  $H_2O_2$  was added to oxidize  $Tc^{4+}$  to  $TcO_4^{-}$ . Then, 6 M NaOH was added to the solution to pH 8-9, and the formed Fe(OH)<sub>3</sub> precipitated was separated by filtration. The filtrate solution with  $TcO_4^-$  was acidified to pH 2–3



Fig. 1 Experiment I – schematic representation of the coprecipitation with  $Fe(OH)_2$  analytical method for Tc determination [24]

using HCl, 20 mg of Fe<sup>3+</sup> (0.2 g L<sup>-1</sup>) and 0.5 g of K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (5 g L<sup>-1</sup>) was added. 6 M NaOH solution was added to adjust pH 9–10, the formed precipitate was separated by filtration on a paper filter. The precipitate was dissolved in 8 M HNO<sub>3</sub>, and 30% solution of H<sub>2</sub>O<sub>2</sub> was added to convert technetium to TcO<sub>4</sub><sup>-</sup>. NaOH was added to adjust pH 9–10, the formed Fe(OH)<sub>3</sub> precipitate was separated by filtration. The filtrate containing TcO<sub>4</sub><sup>-</sup> was acidified to 0.1 M HNO<sub>3</sub>, the sample solution was loaded to a TEVA column (2 mL) which was conditioned with 0.1 M HNO<sub>3</sub>, after rinsing with 40 mL of 1 M HNO<sub>3</sub>, the flow rate of 1.0 mL min<sup>-1</sup> was applied and controlled using a vacuum box. The procedure is shown schematically in Fig. 2.

Separation of  $^{99}$ Tc using TEVA column with increased Fe carrier (Method III).

A modified procedure of Method II was used by increasing the amount of iron(III) to 80 mg  $L^{-1}$  and  $K_2S_2O_5$  to 0.4 g  $L^{-1}$  for co-precipitation of technetium. Meanwhile, the co-precipitation was carried out once. In addition, the sample solution was prepared in a medium of pH 10 for loading, and the column was rinsed using 40 mL of 1 M HNO<sub>3</sub>. Afterward, technetium was eluted with 10 mL of 8 M HNO<sub>3</sub>. The eluate was evaporated at 75 °C to <5 mL, diluted with water. This solution was evaporated to <0.5 mL and transferred to vial with water for LSC measurement. The procedure is shown schematically in Fig. 3.



Fig. 2 Experiment II – schematic representation of the coprecipitation with  $Fe(OH)_2$  analytical method for Tc determination [13]



Fig. 3 Experiment III – schematic representation of the coprecipitation with  $Fe(OH)_2$  analytical method for Tc determination

Sequential separation of U, Pu, Am and Tc from water samples (Method IV).

Tracer solution of  $^{241}$ Am,  $^{239}$ Pu,  $^{233}$ U and  $^{99}$ Tc were spiked to 4 L of simulated sea water and freshwater. The actinides were separated from Tc in the Fe(OH)<sub>3</sub> precipitation [25–27]; the coprecipitate of actinides with Fe(OH)<sub>3</sub> was dissolved in concentrated HCl for subsequent separation of each actinide using TEVA and TRU chromatography (Fig. 4).

# Separation of <sup>99</sup>Tc from real water samples using TEVA column

A modified procedure (Method III) was used to concentrate <sup>99</sup>Tc from environmental water samples collected from Japan Sea and Khanka Lake. Tracer solution of 250 Bq of <sup>99m</sup>Tc was spiked to the 50 L (it was 8 barrels per 50 L) of fresh and sea water which were previously acidified to pH 2



Fig. 4 Schematic representation of simultaneous actinides and technetium separation

using concentrated HCl solution. 4 g of Fe<sup>3+</sup> and 20 g of  $K_2S_2O_5$  were added to each barrel to reduce Tc to Tc(IV), Pu to Pu(III) and Np to N(IV). Concentrated ammonia solution was added to adjust pH to 8-9 and precipitate Tc and actinides with Fe(OH)<sub>2</sub>. After the precipitate was settled by gravity over night, the supernatant was discarded, and the precipitate was separated by filtration. The separated precipitate was dissolved with concentrated HCl solution, and 37% H<sub>2</sub>O<sub>2</sub> was added to oxidize Tc<sup>+4</sup> to TcO<sub>4</sub><sup>-</sup>, meanwhile to oxidize Pu(III) to Pu(IV) and  $Fe^{2+}$  to  $Fe^{3+}$ , any possible <sup>99</sup>Tc assocated organic particles in the precipitate was also decomposed. The concentrated ammonia solution was then added to the sample solution adjust pH to 8-9 to coprecipitate actinides as hydroxides with Fe(OH)<sub>3</sub>, but remain <sup>99</sup>TcO4<sup>-</sup> in the supernatant. The copreciptiate was separated using vacuum filtration and washed two times with 10 mL of milli-Q water. The washes was combined with supernatant, which was loaded to TEVA columns (2 mL) preconditioned with 15 mL of 0.1 M HNO<sub>3</sub>, the column was then rinsed with 10 mL of mili-Q water, 0.5 M HNO3 and 0.5 M NaOH to remove matrix elements and possible interfering elements and radionuclides, 99Tc remaining on the column was finally eluated with 20 mL of 8 M HNO<sub>3</sub> solution. Chemical yield was measured by counting 99mTc spiked to the sample solution in the beginning with  $\gamma$ -spectrometry.

Measurement.

A Tri-Carb 2810TR liquid scintillation spectrometer was used for measurement of <sup>99</sup>Tc separated from the spiked water sample. All eluates with Tc were evaporated at 60°C to less than 0.5 mL, then transferred to 20 mL vial with H<sub>2</sub>O, mixed with 10 mL of Ultima gold<sup>TM</sup> scintillation cocktail from PerkinElmer Inc. and measured. For calculating of efficiency, the quenching curve was obtained. The spectra were processed using the SpectraDec software. <sup>99</sup>Tc separated from environmental water samples was measured using ICP-MS.

Actinides analysis was performed using alpha-spectrometry (multichannel alpha-spectrometer with semiconductor detector Alpha-Ensemble-2). The efficiency for the detection of actinides using an alpha spectrometer is 0.17.

Activity of <sup>99m</sup>Tc was measured with ORTEC GEM-C5060P4-B gamma spectrometer possessing an HPGe semiconductor detector with a beryllium window (relative efficiency of 20%).

The measurement uncertainty includes random errors during the experiments (dispenser error, weighing error, losses during the transfer from beaker to a beaker, losses during filtration, etc.) and instrumental error in measuring activity. The total experimental error includes: statistical counting error (instrumental error) 0.2-2%, volume measurement error 1-3%, random measurement uncertainty standard deviation and relative statistical uncertainty results (0.03-7.7%). In total, the error did not exceed 8% of the obtained results.

## **Results and discussion**

To solve the gap for a combined methodology for Tc and actinides, we choose the co-precipitation with Fe(II). This method is based on the coprecipitation of insoluble forms of technetium(IV) with iron(II) hydroxide Fe(OH)<sub>2</sub>. Various reducing agents can be used to reduce technetium: FeSO<sub>4</sub> [12], hydrazine [28], sulfite anion, etc. [13]. As a source of iron(II) one can use either FeCl<sub>3</sub>, which is reduced simultaneously with technetium, or FeSO<sub>4</sub> which itself serves as a reducing agent. After coprecipitation, the precipitate is separated, iron and technetium are oxidized to  $Fe^{+3}$  and  $Tc^{+7}$ , Fe<sup>+3</sup> is precipitated in the form of Fe(OH)<sub>3</sub> and separated. The chemical yield of technetium separation was 60-75% [13]. For calculating of registration efficiency the quenching curve was obtained (Fig. 5) by measuring a standard solution with different quench levels. CCl<sub>4</sub> was chosen as chemical quencher.

The performance of three procedures for separation of <sup>99</sup>Tc from water samples is presented in Table 2.

High recovery of <sup>99</sup>Tc (90–96%) was obtained for seawater and freshwater samples in the first procedure. Although anion exchange chromatography has been applied for separation of technetium, as well as for uranium, plutonium, neptunium and americium separately [29–31], but a joint separation procedure wasn't reported for sequential separation of actinides and technetium. For the separation of technetium using anion exchange chromatography, the matrix elements and interfering radionuclides and stable isotopes (e.g. <sup>98</sup>MoH<sup>+</sup>, <sup>99</sup>Ru) can be well removed due to the very



Fig. 5 Quenching curve for 99Tc measurement with Tri-Carb 2810TR

 Table 2 Chemical yield of <sup>99</sup>Tc in the separation procedure from fresh and sea water samples (500 mL)

Method	Model solution	Received precipitate volume, mL	Recov- ery of <sup>99</sup> Tc, %
I	Sea water	250	96 ± 8
	Freshwater	250	$90 \pm 7$
II	Sea water	30	$12 \pm 5$
	Freshwater	23	< 5
III	Sea water	40	$46 \pm 6$
	Freshwater	40	$48 \pm 6$

high affinity of  $TcO_4^-$  on the column compared to other elements, and interfering species can be eliminated by rinsing with different elutants (e.g. diluted acid and alkaline solution with complex reagents: washed with water, diluted acid including HNO<sub>3</sub>, and HCl to remove the remained cations and most of anions). In earlier works, <sup>99</sup>Tc on the column was eluted by NaClO<sub>4</sub> and Na<sub>2</sub>SO<sub>3</sub> solution [18]. In step of purification all cations and matrix components can be removed. Thus the advantage of this technique is that anion exchange resin is much cheaper compared to the extraction chromatographic resin, therefore a low cost for the analysis. In addition, anion exchange chromatography is also simple to operate for large amount of loading solution employing a large column, so suitable for separation of technetium and actinides from large volume of water samples. However, a problem to consider is the large amount of the  $Fe(OH)_2$ coprecipitate (250 mL) was obtained, which makes the analysis of large volume of water sample up to 100 L hard to work because of the problem to handle a large amount of precipitate and preparation solution for chromatographic separation. This should be attributed to the amount of FeSO<sub>4</sub> added as carrier for co-precipitation is too high.

In the second procedure, although the amount of precipitate was significantly reduced, and suitable to handle large volumes of water samples, the obtained recoveries of <sup>99</sup>Tc (5-12%) for sea and freshwater samples were very low. The redox potential of  $TcO_4^{-}/TcO_2$  and  $Fe^{3+}/Fe^{2+}$  is 0.782 and 0.770 V, respectively; therefore, the end of the technetium reduction process can be observed by the color change of the solution from orange Fe<sup>3+</sup> to almost dumb or pale green  $Fe^{2+}$ . Since iron has a lower redox potential, technetium is reduced the first, and then iron. Thus, by the change in the color of iron, we can see the completeness of the technetium reduction reaction. It was observed that when a high concentration of NaOH (e.g., 6 mol  $L^{-1}$ ) was added to seawater to adjust the pH to 9-10, white precipitates was also formed, which might be Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>, causing a large amount precipitate and consequently large amount of loading solution in the following chromatographic separation. Ammonia can be used instead of NaOH in order to avoid precipitation of  $Mg(OH)_2$  [13].

Extraction chromatography with a 2 ml TEVA column was used for the separation of technetium in this procedure. It has been tested that technetium can be separated by directly loading the alkaline supernatant from the precipitation of Fe<sup>3+</sup> to the column without acidification, so shortening the procedure. The low recovery of technetium in this procedure might be attributed to the incompletely co-precipitation of technetium due to insufficient amount of iron  $(8 \text{ mg L}^{-1})$  added to the sample. In addition, due to the low concentration of iron carrier, the reduction process technetium could not ensure from the color of iron carrier, because the low concentration of iron makes the color change from Fe<sup>+3</sup> to Fe<sup>2+</sup> is not visible. Therefore, the low chemical yield of technetium might be also attributed to the incompletely reduction of TcO<sub>4</sub><sup>-</sup> to TcO<sub>2</sub>. For preconcentrated technetium from large volumes of natural samples, this procedure needs to be further improved.

In the measurement of <sup>99</sup>Tc by mass spectrometry, e.g., ICP-MS, it is important to take into account the isobaric interference of <sup>99</sup>Ru and polyatomic ion interference of <sup>98</sup>Mo<sup>1</sup>H, because their similar chemical properties with technetium and much high concentrations in the environmental samples as stable isotopes of ruthenium and molybdenum. Molybdenum and ruthenium could follow technetium during the preconcentration and are enriched together with technetium in the loading solution. For large volume seawater samples, were shown that one small TEVA column (1.5 mL resin) is not enough to quantitatively remove molybdenum and ruthenium, but with two TEVA columns, almost all the ruthenium and most of the molybdenum can be removed while technetium is still retrieved in a high chemical yield the molybdenum can be removed while technetium is still retrieved in a high chemical yield [13]. Also we used a vacuum box system with TEVA resin (and we can set the resin cartridge one by one) which makes procedure much shorter and, thus, more profitable for working with a large volume and number of samples.

Based on the results obtained in the first two experiments, the separation procedure was modified by adjusting the amounts of iron carrier and reductant. During the experiment, a sufficient amount of precipitate was obtained for operation (concentration from the initial volume by 10–15 times), and a color change was observed in all reduction and oxidation reactions. In experiment III, the technetium yields improved to be  $46 \pm 6\%$  for seawater and  $48 \pm 6\%$  for freshwater. Technetium purification using TEVA resin from alkaline solutions showed a satisfied recovery of more than  $95(\pm 5)\%$ . The result obtained agrees with the dependence graphs of the resin capacity factor (k') on the acid concentration, which shows that the lower the acidity, the higher the k' [32]. There are two main separation stages in the technetium determination - coprecipitation and chromatographic

separation [18]. The main losses occur in the first stage; therefore it is important to precipitate as much of the radionuclide as possible with a small amount of precipitate for good yields in further separation steps. When working with chromatographic separation, the flow rate is very important to avoid the loss of technetium in this step. In the optimized procedure, a flow rate of 1-2 ml min<sup>-1</sup> was used for loading, rinsing and elution steps. When using ammonia instead of 6 M NaOH for the iron hydroxide precipitation, it is possible to get rid of the magnesium and calcium precipitation, which concentration is high in seawater. In this case, an increased amount of iron carrier is necessary, since the precipitate amount becomes much less in comparison with II. This method is suitable for both seawater and freshwater samples [13]. To improve the chemical vield of technetium in the precipitations step, a further increase of the iron carrier to 0.08 g L<sup>-1</sup> is recommended. All reactions with color change help in the work to understand the completeness of the process, which is very important when working with large volumes and uniqueness of samples. This procedure allows to reduce the operating time with good yields (8 h for 0.5 L samle and 16 h - for 50 L) and can be applied for determination of low technetium in large volumes of natural water.

For simultaneous determination of actinide isotopes with <sup>99</sup>Tc (experiment **IV**), the coprecipitation of technetium was also applied for pre-concentration of actinides and tested by spiking <sup>99</sup>Tc and actinide tracers (<sup>241</sup>Am, <sup>239</sup>Pu, <sup>233</sup>U) into water sample using the procedure **III**. The second precipitate of Fe(OH)<sub>3</sub> was used for sequential separation of U, Pu and Am using combined TEVA-TRU columns. The experiment was carried out 2 times on small volumes -1 L and twice on model solutions with a volume of 5 L. The results of the joint actinides and technetium separation from the spiked sea and freshwater sample according to the modified procedure show good chemical yields (Table 3), which makes it possible to use this technique for simultaneous determination of <sup>99</sup>Tc, isotopes of Pu and U and <sup>241</sup>Am in large volume of natural water samples.

Actinides co-precipitation with iron hydroxide for their further separation is a common preconcentration method from water samples [5, 33]. The high sorption capacity of iron hydroxides contributes to the actinides precipitation with both Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub>. Actinides are quantitatively co-precipitated with Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub> with recoveries of 97–99% [34]. This fact makes it possible to co-precipitation of Tc and actinides from large volume water samples. For better separation of <sup>99</sup>Tc, it is important to convert Tc<sup>4+</sup> in the Fe(OH)<sub>2</sub> precipitate step to TcO<sub>4</sub><sup>-</sup> before separation of Tc from actinide. This is implement with H<sub>2</sub>O<sub>2</sub> in acidic medium. Since H<sub>2</sub>O<sub>2</sub> is not stable at room temperature, employing effective H<sub>2</sub>O<sub>2</sub> is important in this step. In this

 
 Table 3
 The results of joint coprecipitation of actinides and technetium

Experiment	Model solution	Yield, %				
-		<sup>241</sup> Am	<sup>239</sup> Pu	<sup>233</sup> U	<sup>99</sup> Tc	
IV	Sea water	-	$62 \pm 3$	$43 \pm 2$	$38 \pm 3$	
	Freshwater	$50 \pm 5$	$67 \pm 3$	$41 \pm 3$	$33 \pm 4$	

step, Pu will be converted to  $Pu^{4+}$ , while uranium remains at  $UO_2^+$  and americium in  $Am^{3+}$ , these species of actinide can be well co-precipitated with Fe(OH)<sub>3</sub> while remaining TcO<sub>4</sub><sup>-</sup> in the supernatant, achieving the separation of technetium from actinides. At the same time, the iron content in the sample does not interfere with the further separation of americium, uranium and plutonium. The main losses in the actinides separation process, in contrast to the technetium separation, occur at the stage of chromatographic separation. The recoveries of actinides (Pu, U, Am) is about 70–90% for standard solid samples [35]. It is very important to carry out this stage carefully to reach maximum yields.

A technique for simultaneously separation of Am, Pu, U, and Tc from the large volumes of natural water (1-200 L) has been developed with yields of 40–70%. All actinides coprecipitated with iron(III) hydroxide was then separated and purified using extraction chromatographic columns (TEVA, TRU) and technetium remaining the supernatant in the second precipitation of Fe(OH)3 was separated using TEVA column.

For the seawater samples, the chemical yields of 38% for technetium, 62% for plutonium, and 43% for uranium were achieved; for the freshwater, similar chemical yields of 33%, 67%, and 41%, respectively were achieved. Technetium was purified and separated using TEVA resin from alkaline solutions according to a standard technique with a yield>95%. The developed procedure is effective. By precipitation of iron(II) hydroxide with ammonia, allows to get rid of calcium and magnesium hydroxide precipitation, by loading alkaline solution from the Fe(OH)<sub>3</sub> precipitation directly to TEVA column, technetium can be separated without acidification of the solution, therefore less time used; by visible color change of Fe<sup>3+</sup> and Fe<sup>2+</sup>, the complete reduction of technetium to Tc<sup>4+</sup> and high precipitation recovery can be achieved. The developed method is applicable for simultaneous determination of actinides isotopes and <sup>99</sup>Tc in both model seawater and fresh water.

Environmental water samples (200 L) of lake water collected from Lake Khanka and 200 L of seawater colected from Japan Sea were analyzed for <sup>99</sup>Tc and isotopes of actinides using the established method (IV). Tc and actinides was first pre-concentrated from water in each plastic 50 L barrels by copreciptiation after reducing Tc to Tc(IV). The prepared sample solution was passed through two TEVA cartridges (2 mL V) to remove interfering elements as described above, and the separated <sup>99</sup>Tc was determined using ICP-MS. The total yield of the technique for <sup>99</sup>Tc monitored by <sup>99m</sup>Tc tracer was  $36\pm6\%$  for 4 replicates, which is in good agreement with the yields we obtained for simulated sample solutions of different volumes. Analysis of real samples once again confirmed the reproducibility of the results and showed that this technique is valid for the separation of technetium from water samples of large volumes.

During the implementation of the methodology adapted by us, we have achieved a reduction work time from 48 to 16 h. Work with large sample volumes was minimized by single precipitation to separate all described radionuclides. Working with convenient amounts (less than 1 L) of the solution is easy to handle and safe when using concentrated acid reagents. During operation, waste is minimized - only wash solutions remain after extraction chromatography.

#### Conclusions

Three different procedures based on preconcentration using coprecipitation with  $Fe(OH)_2$  and a subsequent purification of Tc with anion exchange and TEVA resins were investigated for separation of Tc. The results showed that the third procedure using  $K_2S_2O_5$  as reductant and two steps precipitation with NH<sub>4</sub> for adjusting pH was more specific. In the pre-concentration step, actinides were also separated from Tc, enable to determine them using the same aliquote of sample after a sequential separation using additional TEVA and TRU column. With this method, we have developed a method for sequential separation and simultaneous determination of U, Pu, Am and Tc isotopes in large volume of seawater and fresh water samples.

With improvement by adjusting the quantity of Fe (III) carrier  $-0.08 \text{ g L}^{-1}$  and reductant  $\text{K}_2\text{S}_2\text{O}_5 - 0.4 \text{ g L}^{-1}$ , a relative good recovery of actinide and technetium was achieved. Meanwhile, the developed method was also shortened by eliminated a few steps such as acidification of the supernatant for separation of <sup>99</sup>Tc, which reduces the operating time.

The developed technique was applied to real water samples from Khanka Lake and Japan Sea. The obtained yields of technetium were  $36 \pm 6\%$ , which is in good agreement with model experiments.

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